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Precisely Embedding Active Sites into a Mesoporous Zr-Framework through Linker Installation for High-efficiency Photocatalysis

Jiandong Pang,[†] Zhengyi Di,^{‡,¶} Jun-Sheng Qin,[§] Shuai Yuan,[†] Christina T. Lollar,[†] Jialuo Li,[†] Peng Zhang,[†] Mingyan Wu,^{*,‡,¶} Daqiang Yuan,^{‡,¶} Maochun Hong,^{‡,¶} and Hong-Cai Zhou^{*,†}

[†]Department of Chemistry, Texas A&M University, College Station, Texas 77843-3255, United States

[‡]State Key Laboratory of Structure Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China

[§]State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, International Center of Future Science, Jilin University, Changchun 130012, China

[¶]University of Chinese Academy of Sciences, Beijing 100049, China

Supporting Information Placeholder

ABSTRACT: The pore engineering of microporous metal-organic frameworks (MOFs) has been extensively investigated in the past two decades and an expansive library of functional groups have been introduced into various frameworks. However, the reliable procurement of MOFs possessing both a targeted pore size and preferred functionality together is less common. This is especially important since the applicability of many elaborately designed materials is often restricted by the small pore sizes of microporous frameworks. Herein, we designed and synthesized a mesoporous MOF based on Zr₆ clusters and tetratopic carboxylate ligands, termed PCN-808. The accessible coordinatively unsaturated metal sites as well as the intrinsic flexibility of the framework make PCN-808 a prime scaffold for post-synthetic modification *via* linker installation. A linear ruthenium-based metalloligand was successfully and precisely installed into the walls of open channels in PCN-808 while maintaining the mesoporosity of the framework. The photocatalytic activity of the obtained material, PCN-808-BDBR, was examined in the aza-Henry reaction and demonstrated high conversion yields after 6 catalytic cycles. Furthermore, thanks to the mesoporous nature of the framework, PCN-808-BDBR also exhibits exceptional yields for the photocatalytic oxidation of dihydroartemisinic acid to artemisinin.

INTRODUCTION

Precise pore environment adjustments in porous materials have been one of the most important topics in materials science because of the significant influence they have on the resulting applicability of the material.¹⁻³ Thanks to their regular and highly tunable pore architectures, the class of porous materials known as metal-organic frameworks (MOFs), or porous coordination networks (PCNs), can be used as intriguing platforms to develop strategies of precise regulation in the pore environments of crystalline solid-state porous materials.⁴⁻⁷ In order to modify the pore interiors of MOFs. introduction of functionalized linkers or groups via onepot synthesis methods and post-synthetic framework decorations are two generally used strategies.⁸⁻¹⁸ Among the most illustrious examples of the one-pot synthesis strategy are the MTV-MOFs developed by Yaghi's group, which have multivariate functionalities assembled from hosting different functional groups.19 linkers Unfortunately, the distribution of the incorporated functional groups in MTV-MOFs are disorganized and therefore difficult to characterized using traditional techniques like X-ray diffraction. In general, the precise

placement of functional groups in one-pot synthesized MTV-MOFs is a huge challenge. Crystallographic disorder can be relieved in the cases of MUF-series MOFs reported by Telfer and co-workers, in which three kinds of linkers with different symmetries are compartmentalized in a predetermined array.²⁰⁻²³ Nonetheless, it is immediately apparent that multiple structures of MOFs can be obtained as impure phases. In addition, the range of chemical functionality within the linkers used in one-pot synthesis is rather limited because the linkers cannot contain functional groups that are thermally labile under the high temperature solvothermal conditions common for MOF syntheses. To a certain degree, a wider range of functionalities can be introduced into MOFs under relatively mild conditions via post-synthetic modification methods. Notwithstanding, the reaction conditions for post-synthetic functionalization of MOFs (including both inorganic and organic transformations) are very hard to control and rely upon the premise that no degradation or collapse of the framework occurs. Furthermore, comprehensive characterization of crystalline powders resulting from post-synthetic methods urgently requires additional developments.9



Figure 1. Construction of the topologically equivalent PCN-608 and PCN-808. (a) The rectangular, planar, 4-connected, tetratopic ligand in PCN-608. (b) The 8-connected Zr_6 cluster in PCN-608 and PCN-808. (c) The expanded rectangular, planar, 4-connected, tetratopic ligand in PCN-808. (d) Crystal structure of PCN-608 viewed along the *c* axis. (e) The **csq** net topology of the mesoporous MOFs, PCN-608 and PCN-808. (f) Crystal structure of PCN-608 viewed along the *c* axis. $R_1 = OH$, NH_2 or OMe, $R_2 = H$ or CF_3 . Color scheme: black, C; red, O; light blue, Zr; yellow, substituents R_1 on the ligands.

Fortunately, our group has developed an alternative method, linker installation, for introducing and precisely placing functional groups into MOFs under mild conditions.²⁴ We have judiciously designed and synthesized a series of Zr-MOFs with 8-connected $Zr_6O_4(OH)_8(H_2O)_4$ clusters as platforms.²⁵ Linear dicarboxylate linkers with distinct lengths and functional groups can be sequentially installed into the platform by replacement of the terminal OH⁻/H₂O ligands on the Zr₆ clusters. Consequently, tailoring of the pore environment in these MOFs was successfully implemented. 26-28 Furthermore, this new strategy can be expanded to mesoporous MOFs, defined as containing pores with diameters between 2 and 50 nm according to the IUPAC notation, which should be more useful for practical applications of the functional groups incorporated. In our previous work it was shown that anionic mesoporous MOFs formed by installation of negatively charged linear linkers can be used to encapsulate cationic [Ru(bpy)₃]²⁺ catalysts by exploiting electrostatic interactions.²⁹ The resulting hybrid material showed high photocatalytic activity and moderate reusability. However, the strength of electrostatic interactions is still too weak to efficiently immobilize the cations, especially in ionizable solvents such as water or in the presence of ionic substrates. Therefore, a more optimized method is desired.

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For more effective immobilization of Ru-containing functional groups, installation of a Ru-containing linker should prove to be a better method. A linear linker, H_2BDBR ($H_2BDBR = [bis(2,2'-bipyridine,N1,N1')(5,5'$ dicarboxy-2,2'-bipyridine-)ruthenium(II)] dichloride), has previously been successfully doped into a H_2BPDC ($H_2BPDC = biphenyl-4,4'-dicarboxylate)-based$ microporous MOF, UiO-67.30-34 As has been mentioned above, the Ru loading amount is usually lower than expected by incorporation of BDBR via one-pot mixed linker synthesis. The characterization of the resulting material remains difficult because of the high level of disorder in mixed linker MOFs as well as the breakage of single crystallinity in the MOFs. What's more, the doping of the photocatalytic active site may block the pores of microporous MOFs, which may be harmful to applicability. Therefore, we tried to synthesize a mesoporous MOF with BDBR incorporated through linker installation. Under the guidance of crystal engineering and reticular chemistry, a mesoporous MOF Zr-based (termed PCN-808, topologically equal to PCN-608) was designed and synthesized (Figure 1). The ditopic linear ligand BPDC and BDBR can be installed and precisely placed into the new mesoporous MOF, which can be characterized demonstratively through single crystal X-ray diffraction. More importantly, the mesoporosity of the MOF as well as the photocatalytic activity of BDBR survive linker installation.

RESULTS AND DISCUSSION

MOF Synthesis and Structural Description. The longer rectangular tetratopic carboxylate ligand H_4 TPTB-H (H_4 TPTB = 5',5'''-bis(4-carboxylatophenyl)-4''',6'dimethoxy-[1,1':3',1'':4'',1''':3''',1''''-quinquephenyl]-4,4'''dicarboxylate) was synthesized similarly to the shorter H_4 TPCB with pre-elongation of the biphenol (Scheme S1). Additionally, H_4 TPTB was obtained when trifluoromethyl groups were introduced to the central phenyl ring, increasing the solubility of the ligand (Scheme S2). Solvothermal reaction of H_4 TPTB and ZrCl₄ in the presence

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of benzoic acid afforded the hexagonal columnar framework complex PCN-808. It should be noted that single crystals suitable for X-ray diffraction can only be obtained when the trifluoromethyl-decorated ligand, TPTB⁴⁻, is employed. Therefore, structural characterization and further linker installation was carried out with the trifluoromethyl-functionalized PCN-808 as representative. Single crystal X-ray diffraction experiments at 100 K show that PCN-808 crystallizes in the hexagonal space group P_6/mmm , which is the same as the PCN-608 series. Each Zr₆ cluster in PCN-808 connects to eight fully 10 deprotonated TPTB⁴⁻ fragments and each TPTB⁴⁻ fragment 11 links to four Zr₆ clusters conversely. The central phenyl 12 ring is approximately perpendicular to the other two 13 lateral phenyl rings in the inner terphenyl part of the TPTB 14 ligand (two sets of disordered phenyl rings were observed 15 with a dihedral angle of 61.63° in reference to the lateral 16 phenyl rings in the single crystal structure). However, the 17 two lateral phenyl rings are inclined to be coplanar and 18 overall the TPTB ligand adopts the $C_{2\nu}$ symmetry necessary 19 to form a csq net framework (Figure S7).35-36 Within the 20 structure, two kinds of one dimensional open channels 21 were formed, i.e. one hexagonal channel with radius of 22 approximately 3.3 nm and one triangular channel with 23 dimensions of approximately 1.2 nm. 24

Tuning the Structure of MOFs by Linker Installation. As shown in Figure 2, the distance between two neighboring Zr_6 clusters along the *c* axis in PCN-608 is about 8.2 Å, while the distance between two neighboring Zr_6 clusters along the *c* axis in PCN-808 is about 11.7 Å due to the elongation of the TPTB ligand. The lengths of linear linkers BDC and BPDC are about 6.9 Å and 11.2 Å respectively, which are all slightly shorter than the open pockets in the mesoporous MOFs. As has been confirmed in our previous research, linker installation of BDC has been successfully implemented into PCN-608 thanks to the inherent flexibility of the framework. The distance between two neighboring Zr_6 clusters along the *c* axis in PCN-608-BDC is about 7.3 Å after BDC is installed. Considering PCN-608 and PCN-808 have the same topology, BPDC and its derivatives are expected to be installable into PCN-808. To prove our hypothesis, linear ligand BPDC and the geometrically equivalent BDBR with a bulky functional group were installed into PCN-808 via single-crystal to single-crystal transformations. The open pockets along the c axis in PCN-808 could be filled with either BPDC or BDBR by incubating crystals in DMF solutions of the appropriate linker, further connecting neighboring Zr₆ clusters through replacement of terminal $OH^{-}/H_{2}O$ ligands. After installation, the c axis contracts from 19.633 Å in PCN-808 to 19.208 Å in PCN-808-BPDC and 19.202 Å in PCN-808-BDBR, thanks to the intrinsic flexibility of PCN-808. Accordingly, the distance between two neighboring Zr_6 clusters along the *c* axis in PCN-808-BPDC and PCN-808-BDBR are also reduced from 11.7 Å to 11.3 Å and 11.4 Å, respectively, which is similar to that of the PCN-608 series (Figure 2). Also similar to that in the PCN-608 series, the 8-connected Zr₆ clusters in PCN-808

become 10-connected nodes in PCN-808-BPDC and PCN-808-BDBR after linker installation (Figure S8).



Figure 2. Crystal structures of (a) PCN-608, (b) PCN-608-BDC, (c) PCN-808, (d) PCN-808-BPDC, and (e) PCN-808-BDBR. (f) Perspective view of PCN-808-BDBR along the c axis. Color scheme: black, C; red, O; light blue, Zr; dark blue, N; pink, Ru; yellow, substituents R_1 on the ligands ($R_1 = OH$, NH_2) or OMe). Trifluoromethyl groups on TPTB ligands omitted for clarity.

In PCN-808-BPDC, the installed linker BPDC can be easily located without disorder. However, the BDBR linker is split into two sets due to the steric effects from the Ru(bpy), group. Both Ru(bpy), parts of the installed ligand point into the hexagonal channels, which may be a benefit in applications like catalysis (Figure 2f). It should be noted that the splitting of BDBR linker in PCN-808-BDBR is different from that of MTV-MOFs. The location of the BDBR linker in PCN-808-BDBR is predesigned and precisely arranged rather than chaotically mixed into solid solutions.

Porosity Analysis and Composition Determination. N₂ adsorption isotherms for PCN-808, PCN-808-BPDC and PCN-808-DBDR were recorded under 77 K and 1 atm to test the porosity of the frameworks before and after linker installation. As shown in Figure 3a, typical type IV sorption isotherms were obtained for all three MOFs with N₂ adsorption decreasing after linker installation, indicative of the mesoporosity of these materials. The Brunauer-



Figure 3. (a) N_2 sorption isotherms of PCN-808 and its derivatives under 77 K and 1 atm. (b) Powder X-ray diffraction (PXRD) patterns of PCN-808 and its derivatives. Note, peaks around 5° move slightly after linker installation.

Emmett–Teller (BET) apparent surface areas for PCN-808, PCN-808-BPDC, and PCN-808-BDBR calculated from the N_2 adsorption data are 2384 m² g⁻¹, 2441 m² g⁻¹, and 1894 m² g⁻¹, respectively. The pore size distribution of PCN-808 and its derivatives were also analyzed by NLDFT methods based on the N_2 sorption data, showing two main pores in PCN-808 series MOFs (i.e. micropores of approximately 1.2 nm and mesopores of approximately 2.5 – 3 nm, Figure S9).

Additionally, powder X-ray diffraction patterns of activated samples and ¹H NMR spectra of digested samples were measured to confirm the phase purity and compositions of the multicomponent MOFs. The PXRD patterns after linker installation are slightly different from those of PCN-808 due to the contraction of the *c* axis. The experimental patterns are consistent with the simulated ones, revealing the phase purity of the MOFs both before and after linker installation (Figure 3b). The linker ratio of TPTB:BPDC in PCN-808-BPDC is about 1:1 according to the ¹H NMR spectra, which is much higher than is calculated based on single crystal data because some of the linear linkers may coordinate to the Zr₆ cluster with only one carboxylate, leaving the other end dangling(Figure S2 and Table S1). Attempts to remove the excess BPDC linkers encapsulated into the mesopores by heating the assynthesized PCN-808-BPDC sample in DMF at 85 °C for 24 hrs and 48 hrs failed. As shown in Figure S4 and S5, the linker ratios of TPTB:BPDC are almost unchanged after treatment, indicating that the excess BPDC linker is hard to remove by washing. However, the linker ratio of TPTB:BDBR in PCN-808-BDBR is about 8:3 according to the ¹H NMR spectra and the Zr:Ru ratio (Zr:Ru = 8:1) from eds mapping, which is a little lower than is calculated from single crystal data and should be ascribed to the steric hindrance of the bulky Ru(bpy)₂ group (Figure S₃ & S₁₂ and Table S1). Although the amount of installed BDBR is slightly lower than the theoretical value, PCN-808-BDBR contains about 17 wt% of BDBR linker which is much

higher than what is obtained from one-pot synthesis of UiO-67-Ru (~ 3 wt%) and similar to that of the postsynthetically produced UiO-67-Ru (~ 15 wt%).^{32, 37} It should be noted that the maximum theoretical value of BDBR linker contents in ideal PCN-808-BDBR and UiO-67-Ru are ~ 22 wt% and ~ 68 wt%, respectively. In other words, the completion of the controllable introduction of BDBR into the frameworks for PCN-808 is much higher than those of UiO-67.

Photocatalysis of the multicomponent MOF. Considering the high porosity of the framework and precisely placed [Ru(bpy)₃]²⁺ sites pointing to the mesopores, PCN-808-BDBR is a good photocatalyst candidate. The one-dimensional open mesopores are suitable for the diffusion of the substrates and the chelated coordination of the BDBR linker is beneficial to the recyclability of the photocatalyst, preventing leakage of the precious metal. A 450 nm LED lamp was selected as the light source for the photocatalytic reactions according to the DR-UV-Vis spectra of PCN-808-BDBR (Figure S 11). In order to investigate the photocatalytic activity of PCN-808-BDBR, the aza-Henry reaction was selected as a model reaction under visible light. As shown in Table 1, the conversion yields of three substrates with different substituents catalyzed by PCN-808-BDBR are similar to those of the free [Ru(bpy)₃]²⁺ cations, indicating that the Ru-immobilized mesoporous MOF is a highly effective photocatalyst. Pristine PCN-808 shows photocatalytic activity for the aza-Henry reactions with conversion yields of 18 % to 33 % which is similar to that of the background reaction in the absence of the photocatalyst reported by Lin and co-workers.³² In order to ascertain the influence of the temperature rise under irradiation, wavelength dependence of the aza-Henry reaction rate on PCN-808-BDBR was also conducted using an 808 nm LED lamp instead of the 450 nm LED lamp with a conversion yield of 28 %, indicating the importance of the photocatalytic

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conditions rather than thermal catalysis on PCN-808-BDBR. In addition, the PCN-808-BDBR catalyst could be recycled with the substrate conversion retaining a value of 93 % after six cycles (Figure S10). Although the photocatalytic activity of PCN-808-BDBR is similar to that of free $[Ru(bpy)_3]^{2+}$, the embedding of the active sites into the frameworks enables facile recycling of this expensive compound.

Table 1. Aza-Henry reactions catalyzed by PCN-808-BDBR



| photocatalyst / conversion (%) ^b | | | | |
|---|-----------------|---------|--------------|--|
| substrate ^a | $Ru(bpy)_3Cl_2$ | PCN-808 | PCN-808-BDBR | |
| 1a | 99 | 27 | >99 | |
| ıb | >99 | 33 | 94 | |
| 1C | >99 | 18 | 99 | |
| | | | | |

^a For the substrate and the product, 1a, 2a, R = H; 1b, 2b, R = Br; 1c, 2c, $R = OCH_3$. ^b Conversion yields were determined by ¹H NMR of the crude product.

It should be noted that the BDBR has been successfully incorporated into microporous UiO-67 and the resulting material (UiO-67-Ru) shows high catalytic activities for aza-Henry reactions.32 However, the small pore size of UiO-67-Ru limits its utility to the photocatalysis of reactions involving large substituents. Compared to UiO-67-Ru, PCN-808-BDBR may be suitable for the photocatalytic reactions of large substituents due to its mesoporous nature. Therefore, PCN-808-BDBR was investigated as a photocatalyst for the photocatalytic oxidation of dihydroartemisinic acid to artemisinin. As shown in Table 2, the conversion and yields of artemisinin catalyzed by PCN-808-BDBR are similar to those of the free $[Ru(bpy)_2]^{2+}$ cations and are much higher than those of PCN-808 and UiO-67-Ru. As expected, large substituents such as dihydroartemisinic can easily diffuse into the mesopores of PCN-808-BDBR where the active sites in the microporous UiO-67-Ru would be inaccessible for such substituents. PXRD patterns were also measured after catalytic tests on PCN-808-BDBR to check the stability of the photocatalyst. The patterns are consistent with the assynthesized ones, suggesting high stability of the material (Figure 3b).

Table2.Photocatalyticoxidationofdihydroartemisinic acid to artemisinin by PCN-808-BDBR



Dihydroartemisinic acid

Artemisinin

| | conversion (%) / yield (%) ^a | | | | |
|--|---|---------|---------|--|--|
| catalyst | run 1 | run 2 | run 3 | | |
| Ru(bpy) ₃ Cl ₂ | >99 / 47 | N.A. | N.A. | | |
| PCN-808 | <5 / <5 | N.A. | N.A. | | |
| UiO-67-Ru | 30 / <5 | N.A. | N.A. | | |
| PCN-808-BDBR | 92 / 42 | 88 / 51 | 90 / 49 | | |
| ^a Conversion yields were determined by ¹ H NMR of the crude product. | | | | | |

CONCLUSIONS

In conclusion, a csq topology mesoporous Zr-MOF, PCN-808, was designedly synthesized through elongation of the tetratopic ligand. The size suitable coordinatively unsaturated pockets as well as the inherent flexibility of the framework play important roles to allow for successful linker installation. A Ru-containing linear linker in addition to a geometrically equivalent linker, BPDC, have been successfully installed into the open pockets of PCN-808. In the resulting mesoporous PCN-808-BDBR, the [Ru(bpy)₃]²⁺ functional groups are precisely placed pointing to the mesopores. Photocatalytic performance of PCN-808-BDBR was examined by aza-Henry reaction with high conversion yields and stability. Furthermore, the mesoporous nature of PCN-808-BDBR makes it suitable for the photocatalytic reactions of large substituents. Our research sheds light on application-oriented, controllable regulations of pore environments in mesoporous MOFs.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge via theInternetathttp://pubs.acs.org.

Text, tables, and figures giving experimental procedures for the syntheses of the ligands, PXRD, N_2 adsorption isotherms, ¹H NMR spectra, and other additional information (PDF)

X-ray crystallographic details of PCN-608 and derivatives (CIF)

X-ray crystallographic details of PCN-808 and derivatives (CIF)

AUTHOR INFORMATION

Corresponding Author

*wumy@fjirsm.ac.cn *zhou@chem.tamu.edu

Notes

The authors declare no competing financial interest.

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